Crosslink Density Measurements in UHMWPE

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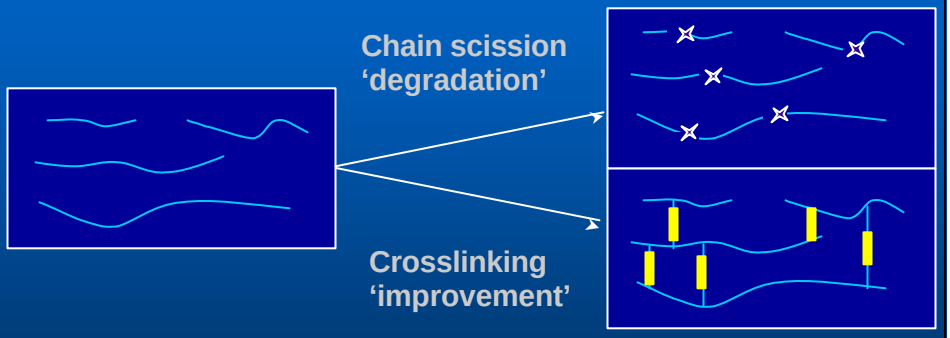
Swelling Measurements

- Quality control tests to monitor consistency of crosslinking
  - through thickness
  - lot to lot
- Quantitative Analysis
  - crosslink density calculation
  - molecular weight between crosslinks

Nomenclature in Radiation Chemistry



G value = # of events (yield) per 100eV or radiation energy

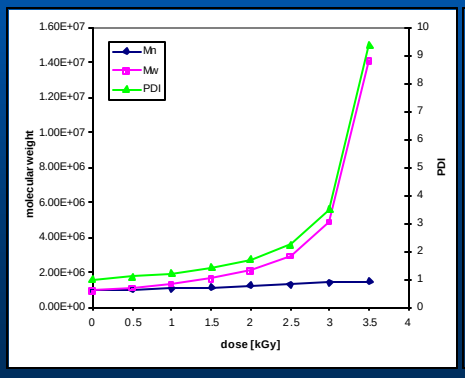
100 eV = 1.602×10^{-17} kGy.g

Radiation Effects on Molecular Weight

$$M_n^{-1} = M_{n,0}^{-1} + [G_s - G_x] D/100 N_{av}$$

$$M_w^{-1} = M_{w,0}^{-1} + [G_s/2 - 2G_x] D/100 N_{av}$$

G(X)=1.4, G(S)=0.5



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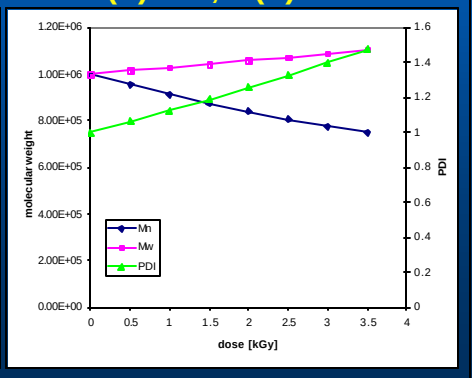
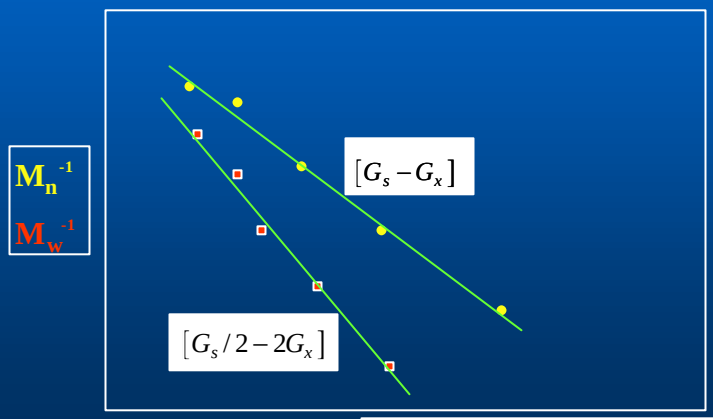


Guven, O., "Crosslinking and Scission in Polymers"

Measuring G-Values

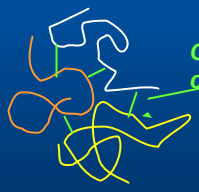
$$M_n^{-1} = M_{n,0}^{-1} + [G_s - G_x]D/100N_{av}$$
$$M_w^{-1} = M_{w,0}^{-1} + [G_s/2 - 2G_x]D/100N_{av}$$



Swelling Studies

- Used to characterize degree of crosslinking in polymer networks
- Competition between free energy of mixing and free energy of elasticity

Polymer chains at rest



In solvent at temperature

Swelling Theory

- Flory, *Principals of Polymer Chemistry* (1953)
- Assumes a tetrafunctional network
  - free ends do not contribute to elastic (retractive) forces

$$\Delta F_m = kT\left[n_1 \ln u_1 + c_1 n \mu_2\right]$$
$$\Delta F_{el} = \left[kTn_e/2\right]\left[3a_s^2 - 3 - \ln a_s^3\right]$$

$$n_d = (-\ln(1-q^{-1}) + q^{-1} + c\,q^{-2})/V_1 q^{-1/3}$$

Measure swell ratio

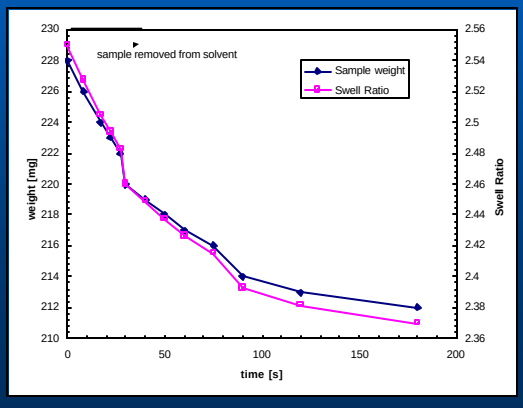
$$q = \left[\frac{V_f}{V_0}\right] = \left[\frac{H_f}{H_0}\right]^3$$

Swelling Studies

Per ASTM D2765

- **Gravimetric approach**

- **Solvent loss**
- **Handling of hazardous hot solvent**

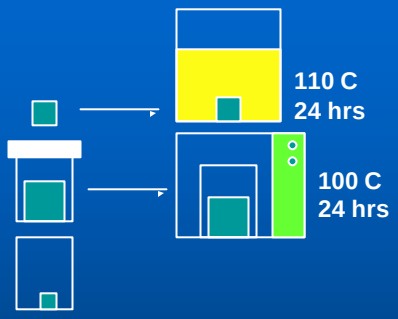


Gravimetric Analysis D2765

Weight dry sample - W_0

Weight swollen gel - W_g

Weight dried gel - W_d



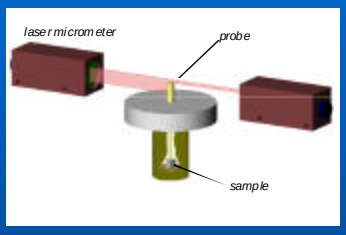
$$q = [W_g - W_d]/[W_d]*K+1$$

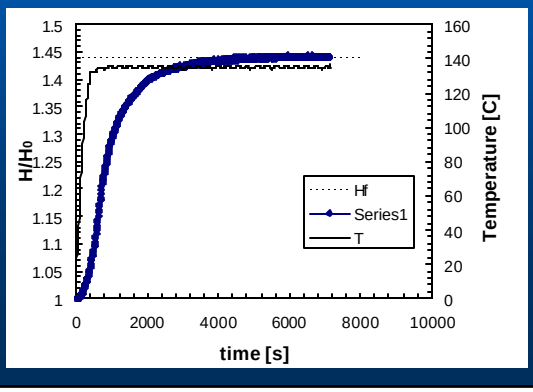
$$\%extract = [W_0 - W_d]/[W_0]*100$$

Swelling Studies

Per new ASTM standard

- **In Situ measurements**
- **Transient and steady state results**
- **Round Robin in progress**



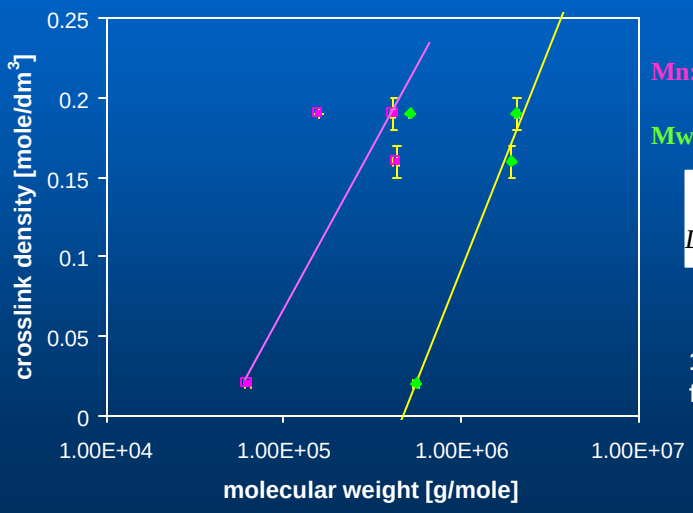


Height Analysis

- Measure initial sample height - H_0
  - o-xylene, 130C
- Monitor transient height H(t) until steady state is reached

- $q = (H_f/H_0)^3$
  - moles of crosslinks/unit volume
  - convert to *Mc* with density

Crosslink density dependence on Molecular Weight

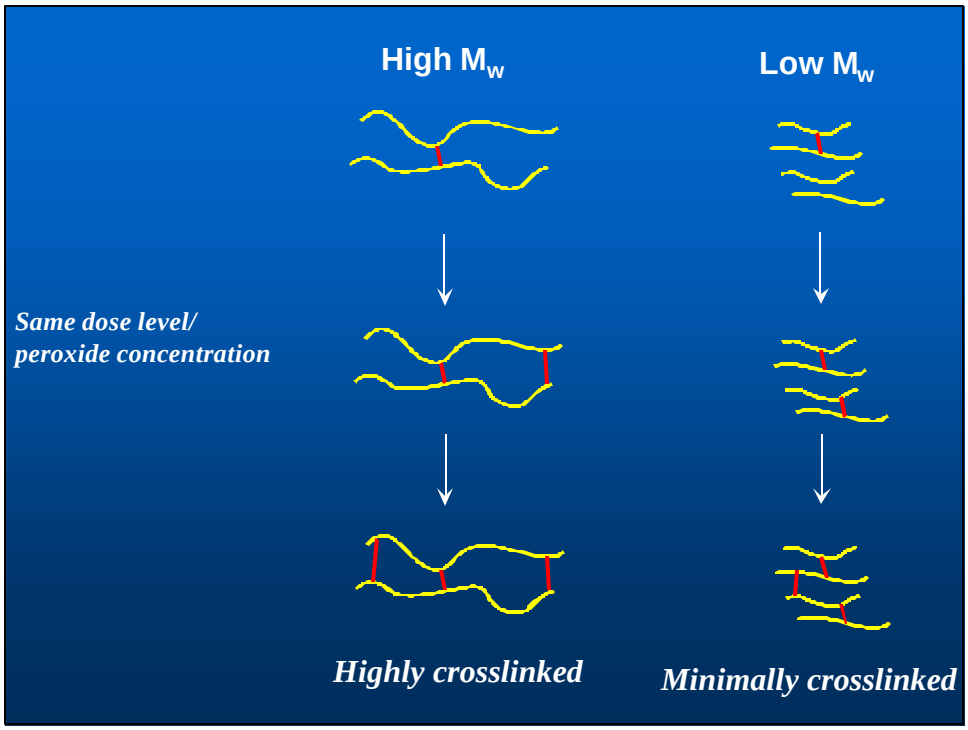


Mn: number-averaged

Mw: weight-averaged

$$D_{gel} = \frac{0.5 \times 10^7}{G(X) M_w}$$

1 kGy required for UHMWPE



Conclusions

- Two techniques for monitoring swelling behavior of UHMWPE
- Provide %gel, crosslink density, swell ratio, molecular weight between crosslinks

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Go to www.campoly.com for application notes on these subjects